

AN EFFORT

TO

REFUTE THE ARGUMENTS ADVANCED

IN FAVOUR OF THE

EXISTENCE IN THE AMPHIDE SALTS, OF RADICALS,

CONSISTING,

LIKE CYANOGEN, OF MORE THAN ONE ELEMENT.

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To Refute the Arguments advanced in Favour of the Existence, in the Amphide Salts, of Radicals consisting, like Cyanogen, of more than one Element. By Robert Hare, M. D., Professor of Chemistry in the University of Pennsylvania.*

The following is a Summary of the Opinions, which it is the Object of the subsequent Reasoning to Justify.

(a) The community of effect, as respects the extrication of hydrogen by contact of certain metals with aqueous solutions of sulphuric and chlorohydric acid, is not an adequate ground for an inferred analogy of composition, since it must inevitably arise that any radical will, from any compound, displace any other radical, when the forces favouring its substitution preponderate over the quiescent affinities.

(b) But if, nevertheless, it be held that the evolution of hydrogen from any combination, by contact with a metal, is a sufficient proof of the existence of a halogen body, simple or compound, in the combination, the evolution of hydrogen from water, by the contact with any metal of the alkalies, must prove oxygen to be a halogen body; also the evolution of hydrogen from sulphydric, selenhydric, or telluhydric acids, by similar means, would justify an inference that sulphur, selenium, or tellurium, as well as oxygen, belong to the halogen or salt radical class:—

(c) The amphigen bodies being thus proved to belong to the halogen class, oxides, sulphides, selenides, and tellurides, would be haloid salts, and their compounds double salts, instead of consisting of a compound radical and a metal:—

(d) The argument in favour of similarity of composition in the haloid and amphide salts, founded on a limited resemblance of properties in some instances, is more than counterbalanced by the extreme dissimilitude in many others:—

(e) As, in either class, almost every property may be found which is observed in any chemical compound, the existence of a similitude, in some cases, might be naturally expected:—

* An amphide salt is one consisting of an acid and a base, each containing an amphigen body, either oxygen, sulphur, selenium, or tellurium, as its electro-negative ingredient.

† The epithet halogen is applied to bodies whose binary compounds with metals are deemed salts, and which are consequently called haloid salts.

(f) As it is evident that many salts, perfectly analogous in composition, are extremely dissimilar in properties, it is not reasonable to consider resemblance in properties, as a proof of analogy in composition:—

(g) No line of distinction, as respects either properties or composition, can be drawn between the binary compounds of the amphiogen and halogen bodies, which justifies that separate classification which the doctrine requires; so that it must be untenable as respects the one, or be extended to the other:—

(h) The great diversity, both as respects properties and composition of the bodies called salts, rendering it impossible to define the meaning of the word, any attempt to vary the language and theory of Chemistry, in reference to the idea of a salt, must be extremely pernicious:—

(i) There is at least as much mystery in the fact, that the addition of an atom of oxygen to an oxacid, should confer an affinity for a simple radical, as that the addition of an atom of this element to such a radical, should create an affinity between it and an oxacid:—

(j) If one atom of oxygen confer upon the base into which it enters, the power to combine with one atom of acid, it is quite consistent that the affinity should be augmented, proportionably, by a further accession of oxygen:—

(k) It were quite as anomalous, mysterious, and improbable, that there should be three oxyphosphions, severally requiring for saturation one, two, and three atoms of hydrogen, as that three isomeric states of phosphoric acid should exist, requiring as many different equivalents of basic water:—

(l) The attributes of acidity alleged to be due altogether to the presence of basic water, are not seen in hydrated acids, when holding water in that form only; nor in such as are, like the oily acids, incapable of uniting with water as a solvent. Further, these attributes are admitted to belong to salts which, not holding water as a base, cannot be hydrurets or hydracids of any salt radical: and while such attributes are found in compounds which, like chromic, or carbonic acid, cannot be considered as hydrurets, they do not exist in all that merit this appellation, as is evident in the cases of prussic acid, or oil of bitter almonds:—

(m) It seems to have escaped attention, that if SO^4 be the oxy-sulphion of sulphates, SO^3 , anhydrous sulphuric acid, must be the oxysulphion of the sulphites; and that there must, in the hyposulphites and hyposulphates, be two other oxysulphions!—

(n) The electrolytic experiments of Daniell have been erro-

neously interpreted, since the electrolysis of the base of sulphate of soda would so cause the separation of sodium, and oxygen, that the oxygen would be attracted to the anode, the hydrogen and soda being *indirectly* evolved by the reaction of sodium with water; while the acid, deprived of its alkaline base, would be found at the anode in combination with basic water, without having been made to act in the capacity of an anion.

(o) The copper in the case of a solution of the sulphate of this metal and a solution of potash, separated by a membrane, would, by electrolyzation, be evolved by the same process as sodium, so long as there should be copper to perform the office of a cathion; and when there should no longer be any copper to act in this capacity, the metal of the alkali, or hydrogen of water, on the other side of the membrane, would act as a cathion; the oxygen acting as an anion from one electrode to the other, first to the copper, and then to the potassium:—

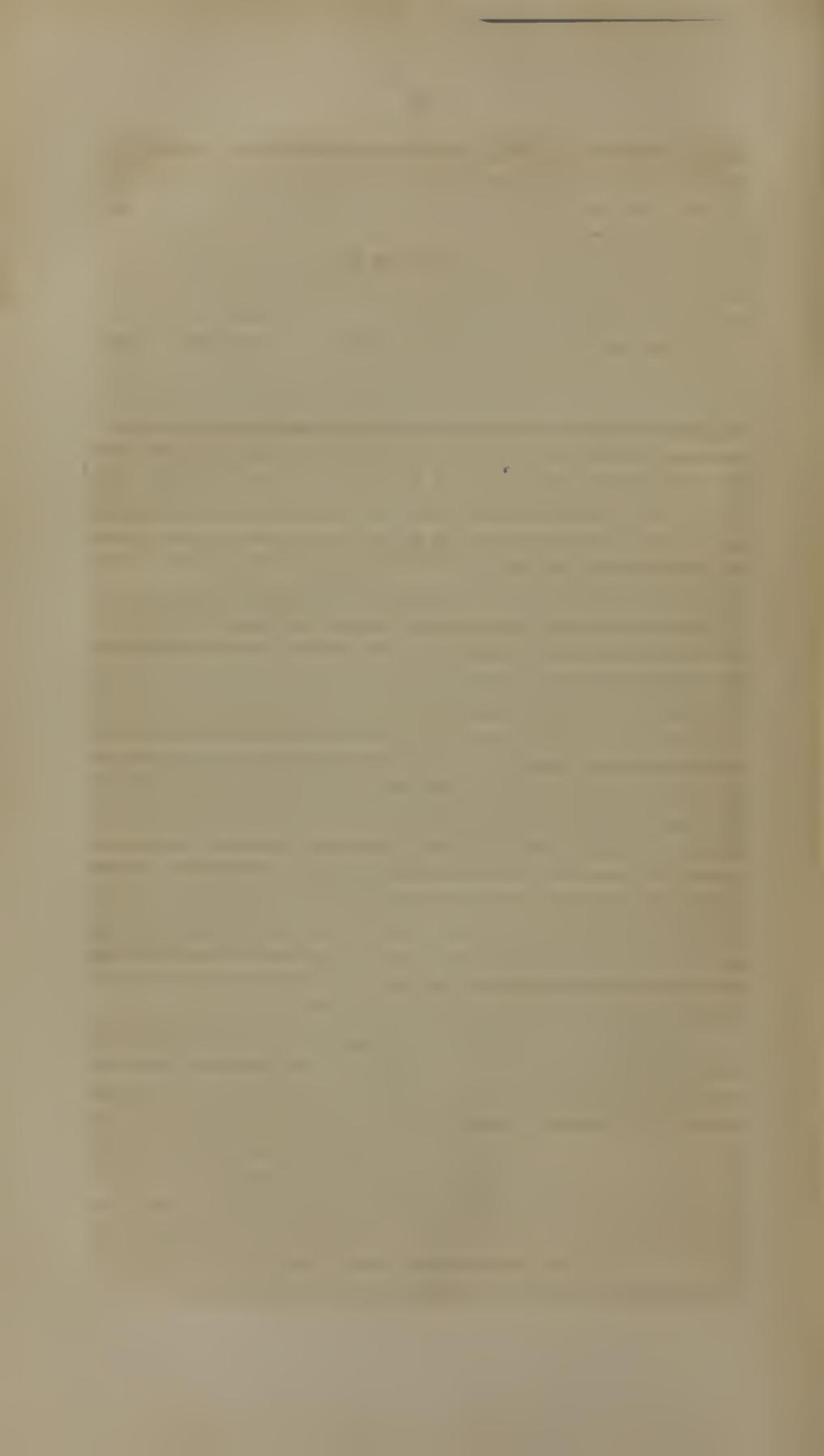
(p) The allegation that the copper was deposited from the want of an anion (oxysulphion) to combine with, is manifestly an error, since, had there been no anion, there could have been no discharge, as alleged, to hydrogen as a cathion, nor any electrolysis:—

(q) The hydrated oxide precipitated on the membrane came from the reaction of the alkali with the sulphate of copper; the precipitated oxide of this metal from the oxygen of the soda acting as an anion; and the deposit of metallic copper from the solutions performing, feebly, the part of electrodes, while themselves the subjects of electrolyzation:—

(r) The so called principles of Liebig,* by which his theory of organic acids is preceded, are mainly an inversion of the truth, since they make the capacity of saturation of hydrated acids dependent on the quantity of hydrogen in their basic water, instead of making both the quantity of water, and, of course, the quantity of hydrogen therein, depend on their capacity:—

(s) All that is truly said of hydrogen would be equally true of any other radical, while the language employed would lead the student to suppose that there is a peculiar association between capacity of saturation, and presence of hydrogen.

* *Traité de Chymie Organique*, tom. 1, page 7.



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&c. &c.

1. Some of the most distinguished European chemists, encouraged by the number of instances in which the existence of hypothetical radicals has been rendered probable, have lately inferred the existence of a large number of such radicals in a most important class of bodies heretofore considered as compounds of acids and bases. It has been inferred, for instance, that sulphur, with four atoms of oxygen (SO^4) constitutes a compound radical, which performs in hydrous sulphuric acid, the same part as chlorine in chlorohydric acid.

2. Graham has proposed sulphatoxygen as a name for this radical, and sulphatoxide for any of its compounds. Daniell has proposed oxysulphion and oxysulphionide for the same purposes. I have given the preference to a nomenclature moulded upon the last mentioned plan. In reasoning on the subject I shall use this nomenclature, not, however, with a view to sanction it, as I disapprove altogether of this innovation, and deny the sufficiency of the grounds upon which it has been justified. Consistently with the language suggested by Daniell, hydrous sulphuric acid, constituted of one atom of acid and one of basic water, (SO^3+HO) is a compound of oxysulphion and hydrogen (SO^4+H). Nitric acid (NO^5+HO) is a compound of oxynitron and hydrogen (NO^6+H). In like manner we should have oxyphosphion in phosphoric acid, oxyarsenion in arsenic acid, and in all acids, hitherto called hydrated, whether organic or inorganic, we should have radicals designated by names made after the same plan. Their salts having corresponding appellations, would be oxysulphionides, oxynitronides, &c. Also, in any salt in which any other of the amphigen class of Berzelius is the electro-negative ingredient, whether sulphur, selenium, or tellurium, all the ingredients excepting the electro-positive radical, would be considered as constituting a compound electronegative radical.*

* The conception of the existence of salt radicals seems to have originated with Davy. It was suggested by Berzelius, in his letter in reply to some strictures which I published on his Nomenclature, in the following language:—

“ If, for instance, the true electro-chemical composition of the sulphate of potash should not be $\text{KO}+\text{SO}^3$, as is generally supposed, but $\text{K}+\text{SO}^4$, and it appears very natural that atoms, so eminently electro-negative as sulphur and oxygen, should be associated, we have, in the salt in question, potassium combined with a compound body, which, like cyanogen in $\text{K}+\text{C}_2\text{N}$, imitates simple halogen bodies, and gives a salt with potassium and other metals. The hydrated oxacids, agreeably to this view, would be then hydracids of a compound halogen body, from which metals may displace hydrogen, as in the hydracids of simple halogen bodies. Thus we know that SO^3 , that is to say, anhydrous sulphuric acid, is a body, whose properties, as respects acidity, differ from those which we should expect in the active principle of hydrous sulphuric acid.

“ The difference between the oxysalts and the halosalts is very easily illustrated

3. It may be expedient to take this opportunity of mentioning, that the advocates of this new view, disadvantageously, as I think, employ the word radical, to designate the electro-negative, as well as the electro-positive ingredient. Agreeably to the nomenclature of Berzelius, the former would be a compound halogen body. Cyanogen being analogous, is by him placed in the halogen class. I shall, therefore, in speaking of "salt radicals," improperly so called, employ the appellation contrived by the great Swedish chemist.

4. It seems, however, to be conceded, that however plausible may be the reasons for inferring the existence of halogen bodies in the amphide salts, it would be inexpedient to make a corresponding change in nomenclature, on account of the great inconvenience which must arise from the consequent change of names.

5. Under these circumstances, it may be well to consider how far there is any necessity for adopting hypothetical views, to which it would be so disadvantageous to accommodate the received language of chemists. In the strictures on the Berzelian nomenclature, which drew from Berzelius the suggestions contained in the quotation at the foot of the preceding page, I stated it to be my impression that water should be considered as acting in some cases as an oxybase, in others as an oxacid; and, in my examination of his reply,* I observed that *hydrous sulphuric acid might be considered as a sulphate of hydrogen, and that when this acid reacts with zinc or iron, the proneness of hydrogen to the aëriform state enables either metal to take its place, agreeably to the established laws of affinity.*

6. There appears to have been a coincidence of opinion between Kane, Graham, Gregory, and myself, as respects the electro-positive relation of hydrogen to the amphigen and halogen elements, which I have designated collectively as the basacigen class; also in the impression that hydrogen acts like a metallic radical, its oxide, water, performing the part of a base. I agree perfectly with Gregory in considering that hydrated acids may be considered as "hydrogen salts." But when the learned editor proceeds to allege that "acids and salts, as respects their constitution, will form one class," I consider him, and those who sanction this allegation, as founding an error upon an oversight. Because the salts of hydrogen, or such as have water for their base, have heretofore been erroneously called acids, we are henceforth to confound salts with acids, and, instead of correcting one wrong name, cause all others to conform thereto!

7. I fully concur with Gregory and Kane, in considering that water in hydrous sulphuric acid, in nitric acid, chloric acid, and in organic acids, generally acts as a base; also, that in this basic water hydrogen performs a part perfectly analogous to that of a metallic radical; but, agreeably to

by formulæ. In KFF (fluoride of potassium), there is but one single line of substitution, that is to say, that of K|FF; whilst in KOOOOS (sulphate of potash) there are two, K|OOOOS and KO|OOOS, of which we use the first in replacing one metal by another, for instance, copper by iron; and the second in replacing one oxide by another.

"I do not know what value you may attach to this development of the constitution of the oxyacids (which applies equally to the sulphoacids and others); but as to myself, I have a thorough conviction that there is therein something more than a vague speculation, since it unfolds to us an internal analogy in phenomena, which, agreeably to the perception of our senses, are extremely analogous."

* Silliman's Journal, Vol. 27, for 1835, page 61.

this view, I cannot perceive any difficulty in accounting for the evolution of hydrogen, as suggested in the quotation above made (6), agreeably to which, when diluted sulphuric acid reacts with zinc or iron, the liberation of hydrogen results from the superiority of the forces which tend to insert either of these metals in the place occupied by the hydrogen, over those which tend to retain it in *statu quo*.

8. When oxide of copper is presented to chlorohydric acid, it is inferred that the hydrogen unites with oxygen, and the chlorine with the metal; and hence it seems to be presumed, that when oxide of copper is combined with sulphuric acid, a similar play of affinities should ensue: but would it be reasonable to make this a ground for assuming the existence of a compound radical, when the phenomena admit of another explanation quite as simple and consistent with the laws of chemical affinity?

9. Whether hydrogen be replaced by zinc, or oxide of hydrogen by oxide of copper, cannot make any material difference. In the one case, a radical expels another radical, and takes its place; in the other, a base expels another base, and takes its place.

10. There can be no difficulty, then, in understanding wherefore, from the compound of sulphur and three atoms of oxygen, and an atom of basic water, hydrogen should be expelled and replaced by zinc, or that water should be expelled and replaced by oxide of copper; the only mystery is in the fact, that SO^3 , as anhydrous sulphuric acid, will not combine with hydrogen, copper, or any other radical, unless oxydized. But this mystery equally exists on assuming that an additional atom of oxygen converts SO^3 into oxysulphion, endowed with an energetic affinity for metallic radicals, to which SO^3 is quite indifferent.

11. In either case an inexplicable mystery exists; but it is, in the one case, associated with an hypothetical change, in the other, with one which is known to take place.

12. But if hydrous sulphuric acid is to be assumed to be a hydruret of a compound halogen body (*oxysulphion*), because it evolves hydrogen on contact with zinc, wherefore is not water, which evolves hydrogen on contact with potassium, sodium, barium, strontium, or calcium, to be considered as a hydruret of oxygen, making oxygen a halogen body?

13. Boldly begging the question, Graham reasons thus: "*the chlorides themselves being salts, their compounds must be double salts.*"

14. But if the chlorides are salts, the chloride of hydrogen is a salt; and if so, wherefore is not the oxide of hydrogen a salt, which, in its susceptibility of the crystalline form, has a salt attribute which the aërisome chloride does not possess?

15. Further, if the oxide of hydrogen be a salt, every oxide is a salt, as well as every chloride. Now, controverting the argument above quoted, by analogous reasoning, it may be said, "*the oxides themselves being salts, their compounds are double salts.*" Of course sulphate of potash is not a sulphatoxide, as Graham's ingenious nomenclature would make it, but must be a double salt, since it consists of two oxides in "*themselves salts.*"

16. I trust that sufficient reasons have been adduced, to make it evident that the common result of the extrication of hydrogen, during the reaction of zinc or iron with sulphuric or chlorohydric acid, is not a competent ground for assuming that there are, in amphide salts, "*compound radicals*" playing the same part as halogen bodies.

17. Let us, in the next place, consider the argument in favour of the ex-

istence of such radicals, founded on the similitude of the haloid and amphide salts, which is stated by Dr. Kane in the following words:—

“ It had long been remarked as curious, that bodies so different in composition as the compound of chlorine with a metal, on one hand, and of an oxygen acid with the oxide of the metal on the other, should be so similar in properties that both must be classed as salts, and should give rise to a series of basic and acid compounds for the most part completely parallel.”—*Elements*, p. 681.

18. Upon the *similitude* and *complete parallelism* of the amphide and haloid salts, thus erroneously alleged, the author proceeds to argue in favour of the existence in the former, of compound halogen bodies, analogous in their mode of combination to chlorine or iodine.

19. I presume it will be granted, that if similitude in properties be a sufficient ground for inferring an analogy in composition, dissimilitude ought to justify an opposite inference. And that if, as the author alleges, certain bodies have been classed as salts, on account of their similarity in this respect, when dissimilar they ought not to be so classed. Under this view of the question, I propose to examine how far any similitude in properties exists between the bodies designated as salts by the author or any other chemist.

20. The salts, hitherto considered as compounds of acids and bases, are by Berzelius called amphide salts, being produced severally by the union with one or other of his amphigen class, comprising oxygen, sulphur, selenium, and tellurium, with two radicals, with one of which an acid is formed, with the other a base. The binary compounds of his halogen class, comprising chlorine, bromine, iodine, fluorine and cyanogen, are called by him haloid salts. I shall use the names thus suggested.

21. Among the haloid salts we have common salt and Derbyshire spar; the gaseous fluorides and chlorides of hydrogen, silicon or boron; the fuming liquor of Libavius; the acrid butyraceous chlorides of zinc, bismuth and antimony; the volatile chlorides of magnesium, iron, chromium, and mercury, and the fixed chlorides of calcium, barium, strontium, silver, and lead; the volatile poison prussic acid, and solid poisonous bicyanide of mercury, with various inert cyanides like those of Prussian blue: likewise a great number of ethereal compounds.

22. Among the amphide salts are the very soluble sulphates of zinc, iron, copper, soda, magnesia, &c., and the insoluble stony sulphates of baryla and strontia; also ceruse and sugar of lead; alabaster, marble, soaps, ethers, and innumerable stony silicates, and aluminates. Last, but not among the least discordant, are the hydrated acids, and alkaline and earthy hydrates.

23. When the various sets of bodies, above enumerated, as comprised in the two classes under consideration, are contemplated, is it not evident that, not only between several sets of haloid and amphide salts, but also between several sets in either class, there is an extreme discordancy in properties: so that making properties the test would involve not only that various sets in one class could not be coupled with certain sets in the other, but, also, that in neither class could any one set be selected as exemplifying the characteristics of a salt, without depriving a majority of those similarly constituted, of all pretensions to the saline character?

24. Now, if among the bodies above enumerated, some pairs of amphide and haloid salts can be selected, which make a tolerable match with respect

to their properties, as in the case of sulphate of soda, and chloride of sodium, while in other cases there is the greatest discordancy, (as in the stony sili-
cate felspar, and the gaseous fluoride fluosilicic acid gas; as in soap and Derbyshire spar; as in marble and the fuming liquor of Libavius, the sour protochloride of tin, and sweet acetate of lead), is it reasonable to found an argument in favour of a hypothetical similitude in composition, on the *resem-
blance* of the two classes in properties? Does not the *extreme* dissimilitude in some cases, more than countervail the limited resemblance in others? And when the great variety of properties displayed both by the amphide and haloid salts is considered, is it a cause for wonder or perplexity, that in some instances, amphide salts should be found to resemble those of the other kind?

25. Again, admitting that there was any cause for perplexity agreeably to the old doctrine, is there less, agreeably to that which is now recommended? Is there no ground for wonder that oxygen or sulphur cannot act as simple halogen bodies? By what rule are their binary compounds to be excluded from the class of haloid salts? Wherefore should chlorides, bromides, iodides, and fluorides, however ant saline in their properties, be considered as salts, while in no case is an oxide, a sulphide, a selenide or telluride to be deemed worthy of that name?

26. I challenge any chemist to assign any good reason wherefore the red iodide of mercury is any more a salt than the red oxide, or the protochloride is more saline than the sulphide: or why the volatile oxides of osmium or of arsenic are less saline than horn silver or horn lead; or the volatile chloride of arsenic, than the comparatively fixed sulphides of the same metal: why gaseous chlorohydric acid is more saline than steam or gaseous oxy-
hydric acid.

27. It much surprises me, that when so much stress is laid upon the idea of a salt, the impossibility of defining the meaning of the word escapes attention. How is a salt to be distinguished from any other binary compound? When the discordant group of substances which have been enumerated under this name is contemplated, is it not evident that no definition of them can be founded on community of properties; and, by the advocates of the new doctrine, composition has been made the object of definition, instead of being the basis; thus, agreeably to them, a compound is not a salt, because it is made of certain elements; but, on the contrary, an element, whether simple or compound, belongs to the class of salt radicals, because it produces a salt. Since sulphur, with four atoms of oxygen, SO_4^4 , produces a salt with a metal, it must be deemed a salt radical.

28. In proof that the double chlorides are not united in a way to justify the opinion adopted by Bonsdorff, Thomson, myself, and others, it is alleged by Graham, "*that in such compounds the characters of the constituent salts are very little affected by their state of union.*"

29. This allegation being, in the next page, admitted to be inapplicable in the case of the double cyanides; an effort is made to get over this obstacle, by suggesting the existence of another compound radical. But the allegation of the author is erroneous as respects various double haloid salts, especially the fluosilicates, the fluoborates, fluozirconiates, the chloroplatinates, chloroiridiates, chloroosmiates, chloropalladiates, &c., all of them compounds in which the constituent fluorides and chlorides exist in a state of energetic combination by which they are materially altered as to their state of existence.

30. Evidently the word salt has been so used, or rather so abused, that

it is impossible to define it, either by a resort to properties or composition; and I conceive, therefore, that to make it a ground of abandoning terms which are susceptible of definition, and which have long been tacitly used by chemists in general, in obedience to such definition, would be "*a retrograde movement in the science.*" I hope Dr. Kane will pardon me for employing the language to which he has resorted, in speaking of the opinions of Bonsdorff.

31. If this doctrine, as it has been stated, is to prevail, I do not perceive how it is to be prevented from claiming an inconvenient extension. The hydrates, as well as the sulphates, must have pretensions to contain salt radicals. Hence in the hydrated alkalies and alkaline earths, there would be a compound radical, consisting of hydrogen, with two atoms of oxygen, hydroxion, and these compounds would be hydroxionides; nor can I conceive that the haloid compounds, erroneously called double salts, but more correctly considered as single salts, can be exempted.

32. Between the reaction of fluoroboric acid with fluobases, and sulphuric acid with oxybases, is there not a great resemblance?

33. I am unable to understand how, if the existence of salt radicals in oxysalts is inferred, the other salts of the amphigen class can be exempted from a corresponding inference. But if the existence of salt radicals in the double sulphides be admitted, can it be consistently denied that they exist also in double chlorides, iodides, &c.? Is there not the greatest analogy between the habitudes of sulphur, selenium, and tellurium, with metals, and those of the halogen bodies?

34. Would not the modification of the etherial oxysalts, to comport with the new hypothesis, be disadvantageous, both as respects our mental conception of those compounds, and the names which would be rendered appropriate? Would not the transfer of the oxygen from the etherial oxide to the acid, and the creation, thus, of new salt radicals for the organic acid salts, be objectionable; such as oxyoxalion for oxalates, oxytartarion for tartrates, oxyacetion for acetates; while, for their compounds, we should have oxyoxalionides, oxytartarionides, oxyacetionides, &c.?

35. If sulphates are to be considered as oxysulphionides, by what names are we to designate the sulphites, hyposulphites, and hyposulphates, SO^2 , S^2O^3 , S^2O^5 ? SO^3 may, perhaps, with more propriety be considered as consisting of a compound radical, SO^2 , and oxygen, forming an oxide of sulphurous acid; but in a sulphite, anhydrous sulphuric acid, SO^3 becomes a species of oxysulphion itself, being as much the oxysulphion of the sulphites, as SO^4 is of the sulphates. Of course SO^3 should have a direct affinity for radicals, contrary to fact. I presume that sulphites would have to be trioxysulphionides; hyposulphites, sesquioxysulphionides; sulphates, quadroxysulphionides; while the hyposulphates would, I suppose, be demiquintoxysulphionides!!!

36. Analogous complication in nomenclature would arise in respect to the nitrites and nitrates, phosphites and phosphates, arsenites and arsenates; also as respects the carbonic, and oxalic acids.

37. It is true that nature has not so made her bodies as that they can be separated into classes, between which any distinct line can be drawn, still it has been found advantageous to classify them to the best of our power. Accordingly it appears to me expedient, in the first place, to distinguish elements (or those compounds which act like them) according to their electro-chemical relations to each other, or their habitudes with the voltaic electrodes. Consistently, chemists have tacitly adopted the plan of

treating the compounds formed by electro-negative elements with anions, as acids; those formed with cathions, as bases; while the combinations formed by the union of such acids and bases have been considered as simple salts. Thus four classes are constituted, consisting of electro-negative elements, of acids, bases, and single salts, while, by the union of the latter, a fifth class of double salts is formed. Whether the words acid, base, and salt, be adhered to, objectionable as they are in some respects, and especially the latter, or some others be contrived, it would seem to me disadvantageous to merge them in one name, pursuant to the views of the advocates of salt radicals, as stated by Gregory in his edition of Turner's Chemistry, 572.

38. The objection, that not being electrolytes the relation of acids and bases to the voltaic electrodes cannot be discovered, is easily remedied; since, on the union of a common ingredient with an anion and a cathion, there cannot be any doubt that the resulting compounds will have the same electro-chemical relation as their respective heterogeneous ingredients; so that, with the anion, an acid or electro-negative body will be formed; with the cathion, a base or electro-positive body. Moreover, as respects organic compounds which cannot be subjected to the electrolytic test, whatever saturates an inorganic acid must be a base, and whatever saturates an inorganic base must be an acid.

39. The word salt, I have shown, is almost destitute of utility, from the impossibility of defining it, and the amplitude of its meaning. A word that means every thing, is nearly as useless as that which means nothing.

40. As respects the three phosphates of water, $\text{PO}^5 + \text{HO}$, $\text{PO}^5 + 2\text{HO}$, $\text{PO}^5 + 3\text{HO}$, the argument used by Dr. Kane cuts both ways; although, by its employer, only that edge is noticed which suits his own purpose. It is alleged that the difference of properties, in these phosphates, is totally inexplicable upon the idea of three degrees of "hydration;" but that all difficulty vanishes, when they are considered as three different compound salt radicals, oxyphosphionides of hydrogen, $\text{PO}^6 + \text{H}$, $\text{PO}^7 + 2\text{H}$, $\text{PO}^8 + 3\text{H}$.

41. To me the formation of three compound elements, by the reiterated addition of an atom, of which five of the same kind were previously in the mass to which the addition is made, seems more anomalous, mysterious, and improbable, than the existence of three compounds of phosphoric acid with water, in which the presence of the different proportions of water is the consequence of some change in the constitution of the elements which is referred to isomerism.

42. No reason can be given why the addition of *one*, *two*, and *three atoms of oxygen*, to the "radical," should convey a power to hold a proportional number of atoms of hydrogen. Such an acquisition of power is an anomaly.

43. In the case of radicals formed with hydrogen in different proportions, as in acetyl and ethyl, formyl and methyl, the number of atoms of oxygen in the peroxides, is the inverse of the hydrogen in the radical.

44. Ethyl, C^4, H^5 , unites, at most, with one atom of oxygen, while acetyl, C^4, H^3 , takes three atoms to form acetic acid, $\text{C}^4, \text{H}^3, \text{O}^3$. Methyl, C^2, H^3 , forms, in like manner, only a protoxide, while formyl, C^2, H , takes three atoms to constitute formic acid.

45. Besides the three oxyphosphions, of which the formulas are above stated, there would have to be another in the phosphites; so that instead of the hydrated acid, or phosphite of water, being $\text{PO}^3 + \text{HO}$, it would have to be $\text{PO}^4 + \text{H}$, a fourth oxyphosphionide of hydrogen.

46. Respecting the new principles which I have been contesting, Dr. Kane alleges "that the elegance and simplicity with which the laws of saline combination may be traced from them is remarkable," because he conceives, that without an appeal to those principles, the fact that the number of equivalents of acid in a salt are proportionable to the number of equivalents of oxygen in the base, would be inexplicable.

47. Thus, when the base is a protoxide, we have one atom of the protoxide of hydrogen to take its place; when the base is a sesquioxide (two of radical and three of oxygen), three atoms of the protoxide of hydrogen take its place: if the base be a bioxide, two atoms of the protoxide of hydrogen take its place.

48. I have already adverted to the existenee of certain chemical laws, inexplicable in the present state of human knowledge. Among these is that of the necessity of oxidation to enable metallic radicals to combine with acids. But as a similar mystery exists as respects the adventitious property of combining with radicals, which results from the aquisition of an additional atom of oxygen by any of the compounds hitherto considered as anhydrous acids, the new doctrine has in that respect no pre-eminent claim to credence.

49. But if, without impairing the comparative pretensions of the prevailing doctrine, we may appeal to the fact that the acquisition of an atom of oxygen confers upon a radical the basic power to hold one atom of acid, is it not consistent that the acquisition of two atoms of oxygen should confer the power to hold two atoms of acid, and that with each further acquisition of oxygen a further power to hold acids should be conferred?

50. So far then there is in the old doctrine no more inserutability than in that which has been proposed as its successor. Since if on the one hand it be requisite that for each atom of oxygen in the base, there shall be an atom of acid in any salt which it may form, on the other, in the case of the three oxyphosphions, for each additional atom of hydrogen extraneous to the salt radical, there must be an atom of oxygen superadded to this radical.

51. It being then admitted that, numerically, the atoms of acid in any oxysalt will be as the atoms of oxygen in the base, it must be evident that whenever an oxysalt of a protoxide is decomposed by a bioxide, there will have to be two atoms of the former for one of the latter. For the bioxide has two atoms of oxygen, and requires by the premises two atoms of acid, while the salt of the protoxide, having but one atom of oxygen, can hold, and yield, only one atom of acid. Two atoms of this salt, therefore, whether its base be water, or any other protoxide, will be decomposed by one atom of bioxide; provided the affinity of the acid for the bioxide predominate over that entertained for the protoxide, as when water is the base.

52. It follows, that the displacement of water from its sulphate, adduced by Kane, does not favour the idea that hydrous sulphuric acid is an oxy-sulphionide of hydrogen, more than the impression that it is a sulphate of water.

53. Of course, in the case of presenting either a sesquioxide, or a trioxide, to the last mentioned sulphate, in other words, hydrous sulphuric acid, the same rationale will be applicable.

54. The next argument advanced by Dr. Kane, is, that *some* of the acids of which the existence is assumed upon the old doctrine, are hypothetical, as they have never been isolated. This mode of reasoning may be made to react against the new doctrine with pre-eminent force, since *all* of the

compound radicals imagined by it are *hypothetical*—none of them having been isolated.

55. The third argument of the respectable author above named is, that acids display their acid character in a high degree only when in the combination with water.

56. This argument should be considered in reference to two different cases, in one of which all the water held by the acid is in the state of a base, while in the other an additional quantity is present acting as a solvent. So far as water, *acting as a solvent*, facilitates the reaction between acids and bases, it performs a part in common with alcohol, ether, volatile oils, resins, vitrifiable fluxes, and caloric. Its efficacy must be referred to the general law, that fluidity is necessary to chemical reaction. “*Corpora non agunt nisi soluta.*”

57. In a majority of cases, basic water, unaided by an additional portion acting as a solvent, is quite incompetent to produce reaction between acids and other bodies. Neither between sulphuric acid and zinc, between nitric acid and silver, nor between glacial or crystallized acids and metallic oxides, does any reaction take place without the aid of water acting as a solvent, and performing a part analogous to that which heat performs in promoting the union of those oxybases with boric, or silicic acid.

58. It is only with *soluble* acids that water has any efficacy. The difference between the energy of sulphuric and silicic acid, under the different circumstances in which they can reciprocally displace each other, is founded on the nature of the solvents which they require, the one being only capable of liquefaction by water, the other by caloric.

59. In support of his opinions the author adverts to the fact, that with hydrated sulphuric acid, baryta will combine energetically *in the cold*, while a similar union between the anhydrous vapour and the same base cannot be accomplished *without heat*. But it ought to be recollect, that to make this argument good, it should be shown wherefore heat causes the baryta, a perfectly fixed body, to unite more readily with an aërisome substance in which increase of temperature must, by rarefaction, diminish the number of its particles in contact with the solid. If the only answer be, that heat effects some mysterious changes in affinity, (or as I would say in the electrical state of the particles) it should be shown that the presence of water or any other base has not been productive of a similar change, before another explanation is held to be necessary. But I would also call to mind that the hydrated acid is presented in the liquid state; and if it be asked why water, having less affinity than baryta, can better cause the condensation of the acid, I reply, that it is brought into contact with the acid both as a liquid and a vapour, of neither of which forms is the earthy base susceptible. But if all that is necessary to convert anhydrous sulphuric acid into an oxysulphionide, be an atom of oxygen and an atom of metal, what is to prevent baryta and anhydrous sulphuric acid from forming an oxysulphionide of barium? All the elements are present which are necessary to form either a sulphate or oxysulphionide; and I am unable to conceive wherefore the inability to combine does not operate as much against the existence of radicals as of bases.

60. I would be glad to learn why, agreeably to the salt radical theory, anhydrous sulphuric acid unites with water more greedily than with baryta, and yet abandons the water promptly on being presented to this base. Why should it form an oxysulphionide with hydrogen more readily than with barium, and yet display, subsequently, a vastly superior affinity for barium?

61. It seems to be overlooked, that anhydrous sulphuric acid, being the oxysulphion of the sulphites, ought to form *sulphites* on contact with metals.

62. But if the sulphate of water owe its energy to that portion of this liquid, which, by its decomposition gives rise to the compound radical oxy-sulphion, and not to the portion which operates as a solvent, wherefore in the concentrated state, will it not react with iron and zinc, without additional water, when, with dilution, it reacts most powerfully with those metals.

63. Some stress has been laid upon the fact, that sourness is not perceived, excepting with the aid of water, as if to derive force for the new doctrine from that old and popular, though now abandoned test of acidity; but it should be recollect that it is not the water which goes to form the compound element in the "*hydracids*," erroneously so called, which confers sourness. Will any one pretend that either sulphuric or nitric acid, when concentrated, is sour? Are they not caustic? Can any of the crystallized organic acids be said to have a sour taste, independently of the moisture of the tongue? The hydrated oily acids being incapable of uniting with water as a solvent, have none of these vulgar attributes of acidity. The absence of these attributes in prussic acid would alone be sufficient to render it inconsistent to consider them as having any connexion with the presence of hydrogen.

64. It has been remarked, that liquid carbonic acid does not combine with oxides on contact. To this I would add, that it does not combine with water under those circumstances, but, on the contrary, separates from it like oil, after mechanical mixture: nor does it, under any circumstances, unite with an equivalent proportion of water to form a hydrate. Of course, as it is not to basic water that it is indebted for its ability to become an ingredient in salts, it cannot be held that this faculty is the result of its previous conversion into an *oxy-carbonide of hydrogen*.

65. Chromic acid is admitted not to require water for isolation, and cannot, therefore, be considered as oxychromionide of hydrogen. Yet the oil of bitter almonds, which consists of a *compound radical*, benzole, and an atom of hydrogen, and which is therefore constituted precisely as the salt radical doctrine requires for endowment with the attributes of an "*hydracid*," is utterly destitute of that acid reaction which hydrogen is represented as peculiarly competent to impart. It follows that we have, on the one hand, in chromic acid, a compound endowed with the attributes of acidity, without being a hydruret of any compound radical; and, on the other, in oil of bitter almonds, a hydruret of a compound radical, without any of the attributes of acidity.

66. The last argument in favour of the existence of salt radicals, which I have to answer, is that founded on certain results of the electrolysis of saline solutions.*

* It is well known that Faraday employed a very simple instrument to ascertain the quantity of the gaseous elements of water yielded in a given time, by a liquid subjected to the voltaic current. It consisted of a graduated tube, through the cavity of which the current was conveyed by wires, so terminating within it, as to have an interval between them through which the current, being conveyed by the electrolytic process, effected the decomposition of the intervening liquid, the resulting gas being caught and measured by the tube. This instrument has been called a volta electrometer, or voltameter.

Faraday found that when various substances were electrolysed, a voltameter being at the same time in the circuit, that for every equivalent of water decomposed within the tube, neither more nor less than an equivalent of the other body could be decomposed.

67. On subjecting a solution of sulphate of soda to electrolysis, so as to be exposed to the current employed, simultaneously with some water in a voltameter, Daniell alleges that, for each equivalent of the gaseous elements of water evolved in the voltameter, there was evolved at the cathode and anode, not only a like quantity of those elements, but likewise an equal number of equivalents of soda and sulphuric acid. This he considers as involving the necessity, agreeably to the old doctrine, of the simultaneous decomposition of two electrolytic atoms in the solution, for one in the voltameter; while, if the solution be considered as holding oxysulphionide of sodium, instead of sulphate of soda, the result may be explained consistently with the law ascertained by Faraday. In that case, oxysulphion would be carried to the anode, where, combining with hydrogen, it would cause oxygen to be extricated, while sodium, carried to the cathode, and deoxidizing water, would cause the extrication of hydrogen.

68. Dr. Kane, alluding to the experiments above mentioned, and some others which I shall mention, alleges that "*Professor Daniell considers the binary theory of salts to be fully established by them.*"

69. Notwithstanding the deference which I have for the distinguished inventor of the constant battery, and disinclination for the unpleasant task of striving to prove a friend to be in the wrong, being of opinion that these inferences are erroneous, I feel it to be my duty, as a teacher of the science, to show that they are founded upon a misinterpretation of the facts appealed to for their justification.

70. It appears to me, that the simultaneous appearance of the elements of water, and of acid and alkali, at the electrodes, as above stated, may be accounted for, simply by that electrolyzation of the soda, which must be the natural consequence of the exposure of the sulphate of that base in the circuit. I will, in support of the exposition which I am about to make, quote the language of Professor Daniell, in his late work, entitled, "Introduction to Chemical Philosophy," page 413:—

"Thus we may conceive that the force of affinity receives an impulse which enables the hydrogen of the first particle of water, which undergoes decomposition, to combine momentarily with the oxygen of the next particle in succession; the hydrogen of this again, with the oxygen of the next; and so on till the last particle of hydrogen communicates its impulse to the platinum, and escapes in its own elastic form."

71. The process here represented as taking place in the instance of the oxide of hydrogen, takes place, of course, in that of any other electrolyte.

72. It is well known, that when a fixed alkaline solution is subjected to the voltaic current, that the alkali, whether soda or potassa, is decomposed; so that if mercury be used for the cathode, the nascent metal, being protected by uniting therewith, an amalgam is formed. If the cathode be of platinum, the metal, being unprotected, is, by decomposing water, reconverted into an oxide as soon as evolved. This shows, that when a salt of potassa or soda is subjected to the voltaic current, it is the alkali which is the primary object of attack, the decomposition of the water being a secondary result.

73. If in a row of the atoms of soda, extending from one electrode to the other, while forming the base of a sulphate, a series of electrolytic decompositions be induced from the cathode on the right, to the anode on the left, by which each atom of sodium in the row will be transferred from the atom of acid with which it was previously combined, to that next upon the right,

causing an atom of the metal to be liberated at the cathode; this atom, de-oxidizing water, will account for the soda and hydrogen at the cathode. Meanwhile the atom of sulphate on the left, which has been deprived of its sodium, must simultaneously have yielded to the anode the oxygen by which this metal was oxidized. Of course the acid is left in the hydrous state, usually called free, though more correctly esteemed to be that of a sulphate of water.

74. I cannot conceive how any other result could be expected from the electrolysis of the base of sulphate of soda, than that which is here described. Should any additional illustration be requisite, it will be found in a note subjoined.*

75. I will, in the next place, consider the phenomena observed by Professor Daniell, when solutions of potassa and sulphate of copper, separated by a membrane, were made the medium of a voltaic current.

76. Of these I here quote his own account. *Philosophical Magazine and Journal*, Vol. 17, p. 172:—

“A small glass bell, with an aperture at top, had its mouth closed by tying a piece of thin membrane over it. It was half filled with a dilute solution of caustic potassa, and suspended in a glass vessel containing a strong

* It is easy to understand how a simultaneous appearance of oxygen and acid at the anode, and soda and hydrogen at the cathode, may ensue, simply by the electrolyzation of the alkaline base from the following association of formulae.

Anhydrous sulphuric acid is represented by the usual formula, SO_3 ; oxygen by the usual symbol, O; sodium by Na; water, acting as a solvent, by HO. Each atom of oxygen, sodium, or acid, is numbered from right to left, 1, 2, 3, 4, so that the change of position consequent to electrolysis may be seen.

	1	2	3	4	Water.	
Anode	O	O	O	O	HO	Cathode.
1		2	3	4		
~~~~~	~~~~~	~~~~~	~~~~~	~~~~~		
Na	Na	Na	Na	Na		
1	2	3	4			
~~~~~	~~~~~	~~~~~	~~~~~	~~~~~		
SO_3	SO_3	SO_3	SO_3	SO_3		
HO	HO	HO	HO	HO		

	1	2	3	4	O	H	Cathode.
Anode	O	O	O	O	O	H	
1		2	3	4			
~~~~~	~~~~~	~~~~~	~~~~~	~~~~~			
Na	Na	Na	Na	Na			
2	3	4					
~~~~~	~~~~~	~~~~~	~~~~~	~~~~~			
SO_3	SO_3	SO_3	SO_3	SO_3			
HO	HO	HO	HO	HO			

As the atoms are situated in the second arrangement, the atom of oxygen (1), is

at the anode, the atom of sodium, Na , with which it had been united, having been transferred to the second atom of sulphuric acid, which had yielded its sodium to the

third atom of acid, SO_3 , this having, in like manner, yielded its sodium to the fourth

atom of acid, SO_3 , from which the fourth atom of sodium, Na , had been abstracted by the electrolytic power. The atom of sodium thus removed from the fourth atom of acid, is represented in union with the oxygen of an atom of water, of which the hydrogen, H, is at the cathode.

neutral solution of sulphate of copper, below the surface of which it just dipped. A platinum electrode, connected with the last zinc rod of a large constant battery of twenty cells, was placed in the solution of potassa; and another, connected with the copper of the first cell, was placed in the sulphate of copper immediately under the diaphragm which separated the two solutions. The circuit conducted very readily, and the action was very energetic. Hydrogen was given off at the platinode in a solution of potassa, and oxygen at the zincode in the sulphate of copper. A small quantity of gas was also seen to rise from the surface of the diaphragm. In about ten minutes the lower surface of the membrane was found beautifully coated with metallic copper, interspersed with oxide of copper of a black colour, and hydrated oxide of copper of a light blue.

"The explanation of these phenomena is obvious. In the experimental cell we have two electrolytes separated by a membrane, through both of which the current must pass to complete its circuit. The sulphate of copper is resolved into its compound anion, sulphuric acid + oxygen (oxysulphion), and its simple cathion, copper: the oxygen of the former escapes at the zincode, but the copper on its passage to the platinode is stopped at the surface of the second electrolyte, which for the present we may regard as water improved in its conducting power by potassa. The metal here finds nothing by combining with which it can complete its course, but being forced to stop, yields up its charge to the hydrogen of the second electrolyte, which passes on to the platinode, and is evolved.

"The corresponding oxygen stops also at the diaphragm, giving up its charge to the anion of the sulphate of copper. The copper and oxygen thus meeting at the intermediate point, partly enter into combination, and form the black oxide; but from the rapidity of the action, there is not time for the whole to combine, and a portion of the copper remains in the metallic state, and a portion of the gaseous oxygen escapes. The precipitation of blue hydrated oxide doubtless arose from the mixing of a small portion of the two solutions."

77. It will be admitted, that agreeably to the admirable researches of Faraday, there are two modes in which a voltaic current may be transmitted, *conduction* and *electrolyzation*. In order that it may pass by the last mentioned process, there must be a row of anions and cathions forming a series of electrolytic atoms extending from the cathode to the anode. It is not necessary that these atoms should belong to the same fluid. A succession of atoms, whether homogeneous, or of two kinds, will answer, provided either be susceptible of electrolyzation. Both of the liquids resorted to by Daniell, contained atoms susceptible of being electrolyzed. If his idea of the composition of sulphate of copper, and the part performed by the potassa, were admitted for the purpose of illustration, we should, on one side of the membrane, have a row of atoms consisting of oxysulphion and copper; on the other, of oxygen and hydrogen.

78. Recurring to Daniell's own description of the electrolyzing process, above quoted, an atom of copper near the anode being liberated from its anion, oxysulphion, and charged with electricity, seizes the next atom of oxysulphion, displacing and charging an atom of copper therewith united. The cupreous atom thus charged and displaced, seizes a third atom of oxysulphion, subjecting the copper, united with it, to the same treatment as it had itself previously met with. This process being repeated by a succession of similar decompositions and recompositions, an electrified atom of copper is evolved at the membrane, where there is no atom of oxysulphion. Were there *no other anion* to receive the copper, evidently the electrolyzation would not have taken place; but oxygen, on the one side of the membrane, must succeed to the office performed by oxysulphion on the other

side; while hydrogen, in like manner, must succeed to the office of the copper.

79. Such being the inevitable conditions of the process, how can it be correctly alleged by Professor Daniell, the transfer of the copper being arrested at the membrane, that as this metal "*can find nothing to combine with*," it gives up its electrical charge to the hydrogen, which proceeds to the cathode? As hydrogen cannot be present, excepting as an ingredient in water, how can it be said that the copper can discharge itself upon the hydrogen, without combining with the oxygen necessarily liberated at the same time by the electrolytic process? How could the copper, in discharging itself to a cathion, escape a simultaneous seizure by an anion? Would not the oxidizement of this metal be a step indispensable to the propagation of that electrolytic process, by which alone the hydrogen could, as alleged, "*pass to the platinode*," i. e. cathode?

80. In these strictures I am fully justified by the following allegations of Faraday, which I quote from his *Researches*, 826, 828:—

"A single ion, i. e. one not in combination with another, will have no tendency to pass to either of the electrodes, and will be perfectly indifferent to the passing current, unless it be itself a compound of more elementary ions, and so subject to actual decomposition."

"If, therefore, an ion pass towards one of the electrodes, another ion must also be passing simultaneously to the other electrode, although, from secondary action, it may not make its appearance."

81. In explanation of the mixed precipitates produced upon the membrane, I suggest that the hydrated oxide resulted from chemical reaction between the alkali and acid, the oxide from the oxygen of the water or potassa acting as a cathion in place of that of the oxide of copper: also that the metallic copper is to be attributed to the solutions acting both as conductors and as electrolytes; so that, at the membrane, two feeble electrodes were formed, which enabled a portion of the copper to be discharged without combining with an anion, and a portion of oxygen to be discharged without uniting with a cathion. In this explanation I am supported by the author's account of a well known experiment by Faraday, in which a solution of magnesia and water was made to act as electrodes at their surfaces respectively.

82. There can, I think, be no better proof that no reliance should be placed on the experiments with membranes, in this and other cases where the existence of compound radicals in acids is to be tested, than the error into which an investigator, so sagacious as my friend Professor Daniell, has been led, in explaining the complicated results.

83. The association of two electrolytes, and the chemical reaction between the potassa and acid, which is admitted to have evolved the hydrated oxide, seem rather to have created difficulties than to have removed them.

84. In this view of the subject, I am supported by the opinion of Faraday, as expressed in the following language:—

"When other metallic solutions are used, containing, for instance, peroxides, as that of copper combined with this or any decomposable acid, still more complicated results will be obtained, which, viewed as the direct results of electro-chemical action, will, in their proportions, present nothing but confusion; but will appear perfectly harmonious and simple, if they be considered as secondary results, and will accord in their proportions with the oxygen and hydrogen evolved from water by the action of a definite quantity of electricity."

85. I cannot conceive, that in any point of view the complicated and "confused" results of the experiment of Daniell with electrolytes separated by membranes, are rendered more intelligible by supposing the existence of salt radicals. I cannot perceive that the idea that the anion in the sulphate is oxysulphion, makes the explanation more satisfactory than if we suppose it to be oxygen. Were a solution of copper subjected to electrolysis alone, if the oxide of copper were the primary object of the current, the result would be analogous to the case of sodium, excepting that the metal evolved at the cathode, not decomposing water, would appear in the metallic form. If water be the primary object of attack, the evolution of copper would be a secondary effect.

86. It is remarkable, that after I had written the preceding interpretation of Daniell's experiments, I met with the following deductions stated by Matteuchi, as the result of an arduous series of experiments, without any reference to those of Daniell above mentioned. It will be perceived that these deductions coincide perfectly with mine.

87. I subjoin a literal translation of the language of Matteuchi from the *Annales de Chimie et de Physique*, tome 74, 1840, page 110:—

"When salt, dissolved in water, is decomposed by the voltaic current, if the action of the current be confined to the salt, for each equivalent of water decomposed in the voltmeter, there will be an equivalent of metal at the negative pole, and an equivalent of acid, plus an equivalent of oxygen, at the positive pole. The metal separated at the negative pole will be in the metallic state, or oxidized according to its nature. If oxidized, an equivalent of hydrogen will be simultaneously disengaged by the chemical decomposition of water."

88. Thus it seems, that the appearance of acid and oxygen at the anode, and of alkali and hydrogen at the cathode, which has been considered as requiring the simultaneous decomposition of two electrolytes upon the heretofore received theory of salts, has, by Matteuchi, been found to be a result requiring the electrolysis of the metallic base only, and, consequently, to be perfectly reconcilable with that theory.

89. In fact I had, from the study of Faraday's Researches, taken up the impression, that the separate appearance of an acid and base, previously forming a salt, at the voltaic electrodes, was to be viewed as a secondary effect of the decomposition of the water or the base; so that acids and bases were never the direct objects of electrolytic transfer.

Of Liebig's "Principles," so called.

90. Under the head of the "theory of organic acids," in Liebig's Treatise on Organic Chemistry, we find the following allegations dignified by the name of principles. Manifestly they must tend to convey a false impression to the student, that hydrogen has a peculiar property of creating a capacity for saturation, instead of being only the measure of that capacity, as is actually true, and likewise that in this respect it differs from any other radical.

91. The allegations to which I refer are as follows, being a literal translation from the French copy of the *Traité de Liebig*, page 7:—

"The hydrated acids are combinations of one or more elements with hydrogen, in which the latter may be replaced wholly or in part by equivalents of metals."

"The capacity of saturation depends consequently on the quantity of hydrogen which can be replaced."

"The compound formed by the other elements being considered as a radical, it is evident that the composition of this radical can exercise no influence on the capacity of saturation.

"The capacity of saturation of these acids augments or diminishes in the same ratio as the quantity of hydrogen, not entering into the salt radical, augments or diminishes.

"If into the composition of the salt radical there should be introduced an undetermined quantity of any elements, without changing the quantity of hydrogen extraneous to the radical, the atomic weight of the acid would be augmented, but the capacity of saturation would remain the same."

92. As by the advocates of the existence of "*salt radicals*," hydrogen is considered as playing the part of a metallic radical, and must, therefore, as respects any relation between it and the capacity of saturation, be in the same predicament as any other electro-positive radical, I cannot conceive wherefore laws, which affect every other body of this kind, should be stated as if particularly associated with hydrogen.*

93. Would not a more comprehensive and correct idea be presented by the following language?—

94. From any combination of an acid with a base, either the base or its radical may be replaced by any other radical or base, between which and the other elements present, there is a higher affinity. Of course from acids called hydrated, from their holding an atom of basic water, either this base, or its radical (hydrogen), may be replaced by any other competent base or radical.

95. The premises being manifestly fallacious, still more so is the subsequent allegation, that in consequence of the hydrated acids being compounds formed with hydrogen, their capacity of saturation *depends* on the quantity of this element which can be replaced.

96. Is not this an inversion of the obvious truth, that the quantity of hydrogen present is as the capacity of saturation; and that, of course, the quantity of any element which can be substituted for it, must be in equivalent proportion? Would not a student, from this, take up two erroneous

* There is, in some respects, a coincidence so remarkable as to the part taken by Dr. Kane and myself, with respect to hydrogen, that I quote here the language which has been held by us respectively on this subject.

Treating of hydrogen, Dr. Kane uses the following words:—"It was at one time supposed that it shared with oxygen the power of generating acids; and as sulphur, chlorine, iodine, cyanogen, &c., formed one class by combining with oxygen, so they formed a second class, called hydracids, by entering into union with hydrogen."

* * * In the year 1832 I proved this view to be incorrect, that all the properties of the compounds of hydrogen combined to show that it was an eminently electro-positive body, that it took place along with iron, manganese, and zinc. * * * * "These views have been still farther corroborated by the researches of Graham." * * * There rests now, no doubt, in the minds of philosophical chemists, that hydrogen is a metal enormously volatile.

This justifies the following language held in my letter on the Berzelian nomenclature.

"I am of opinion that the employment of the word hydracid, as co-ordinate with oxacid, must tend to convey the erroneous idea, with which, in opposition to his own definition, the author seems to have been imbued, that hydrogen in the one class, plays the same part as oxygen in the other. But in reality, the former is eminently a combustible, and of course the radical, by his own definition."

So entirely have I concurred in considering hydrogen as an aëroform metal, that, for more than twenty years, I have, in my lectures, accounted for the amalgamation of mercury when electrolysed in contact with sal ammoniac, by inferring ammonia to be a gaseous alloy of two metallic ingredients, hydrogen and nitrogen being both aëroform metals.

ideas—first, that the capacity of saturation is conferred by the radical, and in the next place, that of all radicals, hydrogen alone can give such a capacity? Is it not plain, that the assertion here made by the celebrated author, would be true of any radical?

97. Passing over a sentence which has no bearing on the topic under discussion, in the fourth allegation we have a reiteration and expansion of the error of those by which it is preceded. We are informed that the "*capacity of saturation augments and diminishes with the quantity of hydrogen which can be replaced*," which is again an inversion of the truth, that the quantity of hydrogen varying with the capacity, the quantity of any other radical, competent to replace it, must be in equivalent proportion.

98. Is not the concluding allegation a mere truism, by which we are informed, "that if any undetermined quantity of any element should be introduced into the composition of the radical, without changing the capacity (as measured by hydrogen), the capacity would be found the same when measured by any other radical?"

99. As all that is thus ascribed to hydrogen must be equally true of any other radical, there would have been less liability to misapprehension, had the generic term radical been employed wherever hydrogen is mentioned. But by employing the word radical to designate halogen elements, the advocates of the existence of compound radicals in amphoteric salts have deprived the word in question of much of its discriminating efficacy. In fact, their nomenclature would confound all ultimate elements under one generic appellation, and all their binary combinations under another, so that almost every chemical reagent, whether simple or compound, would be a salt or a radical.

100. Before concluding, I feel it to be due to the celebrated German chemist above mentioned, to add, that however I may differ from him as to the acids being hydrurcts of compound radicals, I am fully disposed to make acknowledgments for the light thrown by his analytical researches on organic chemistry, and the successful effect of his ingenious theoretic speculations, in rendering that science more an object of study with physicians and agriculturists.

AN ABSTRACT

From Kane's Elements, of the Arguments in Favour of the Existence of Compound Radicals in Amphide Salts.

It appears proper to give the student of this text book, the option of studying the arguments which it is the object of the preceding pages to refute. Hence I subjoin the following abstract from Kane's Elements, page 681:—

"It had been long remarked as curious, that bodies so totally different in composition as the compound of chlorine with a metal on the one hand, and of an oxygen acid with the oxide of the metal on the other, should be so similar in properties, that both must be classed together as *salts*, and should give origin to series of basic and acid compounds for the most part completely parallel. This difficulty has been so much felt by the most enlightened chemists, that doubts have been raised as to whether the acid and base, which are placed in contact to form by their union an oxygen salt, really exist in it when formed; and it has been suggested, that at the moment of union a new arrangement of elements takes place, by which the structure of the resulting salt is assimilated to that of a compound of chlorine or of iodine with a metal. This view, at first sight so far-fetched, which considers that in glauber's salt there is neither sulphuric acid, nor soda, but sulphur, oxygen, and sodium, in some other and simpler mode of combination, is now very extensively received by chemists; and I shall proceed, therefore, to describe with some detail the form which it has assumed, and the evidence by which it is supported.

The greater number of those bodies which are termed oxygen acids, have not been in reality insulated, and what are popularly so called are merely supposed to contain the dry acid combined with water. Thus the nearest approach we can make to nitric acid, is the liquid NO_3H ; to acetic acid, the crystalline body $\text{C}_4\text{H}_4\text{O}_4$; and to oxalic acid, the sublimed crystals $\text{C}_2\text{O}_4\text{H}$; we look upon these bodies as being combinations of the *dry acid* with water, and we write their formulæ $\text{NO}_3 + \text{HO}$, and $\text{C}_4\text{H}_4\text{O}_4 + \text{HO}$ and $\text{C}_2\text{O}_4 + \text{HO}$, but that these dry acids exist at all is a mere assumption. Hence with regard to these instances, and they embrace the majority of all known acids, the idea that the acid and base really exist in the salt formed by the action of hydrated acids on a base, is purely theoretical.

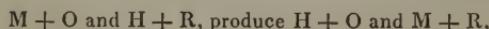
When we compare the constitution of a neutral salt with that of the hydrated acid by which it is formed, we find the positive result to be the substitution of a metal for the hydrogen of the latter, thus, $\text{SO}_3 + \text{HO}$ gives with zinc $\text{SO}_3 + \text{ZnO}$; and where a metal is acted on by an hydrated acid, the hydrogen is thus evolved either directly as gas, or it reacts on the elements of the acid and gives rise to secondary products which are evolved, such as sulphurous acid, nitric oxide, &c. In all cases we may consider the action of a metal on a hydrated acid, to be primarily the elimination of hydrogen and the formation of a neutral salt. But in this respect the action becomes completely analogous to that of the metal on a hydracid, except that in the latter case a haloid salt is formed, and hence we assimilate the two classes in constitution by a very simple arrangement of their formulæ.

There are, however, a number of acids which may be obtained in a dry and isolated form, as the sulphuric, the silicic, the telluric, the stannic, the arsenic, the phosphoric, &c., and when they combine with bases, it is most natural to consider the union as being direct, and that the salt contains acid and base really as such. This is accordingly the strongest point of the ordinary theory. But other and important circumstances intervene. These acids, although they may be obtained free from water, yet in that state they combine with bases but very feebly, and require a high temperature in order to bring their affinities into play. On the other hand, in all cases where these bodies manifest their acid characters in the highest degree, they are combined with water, as in oil of vitriol and phosphoric acid, and when expelled from combination with a base, they immediately enter into combination with water in an equivalent proportion. Thus where phosphate of lime is decomposed by oil of vitriol, it is not phosphoric acid (PO_3) which is found in the liquor, but its

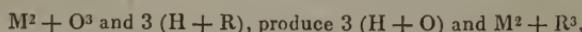
terhydrate ($\text{PO}_5 + 3\text{HO}$), as is shown by its forming with oxide of silver the yellow phosphate $\text{PO}_3 + 3\text{AgO}$. In the case of telluric acid, its hydrate ($\text{TeO}_3 + 3\text{HO}$) is very soluble in water, it crystallizes in large prisms; by 212° two atoms of water are given off, but its nature is not changed, the body which remains ($\text{TeO}_3 + \text{HO}$) is still acid and soluble in water, perfectly neutralizing the alkalies; but by a red heat this last atom of water is driven off, and then the whole nature of the body changes, it is insoluble in water, and even in the strongest alkaline solutions, and can only be brought back to its former state by being fused with potash at a red heat. Here it is evident that the acid properties and the water go together; and we may conclude, that in order to manifest strong acid properties, the acid must be in its hydrated form. But in that hydrated form, if the water acted as a base simply, the tendency of the acid to combine with other bases should be inferior to that of the dry acid; for if we place oil of vitriol and barytes together, the water must be first expelled, before the barytes and sulphuric acid can unite, and hence an impediment would exist to their union which should not occur with cold barytes and dry sulphuric acid in vapour, and yet cold barytes and oil of vitriol will combine with such intensity as to produce ignition, whilst the barytes must be heated before it begins to combine with the dry sulphuric acid. The water, therefore, is essential to the manifestation of strong acid properties, and it does not exist in combination with the acid merely as a base. What, then, is the constitution of a hydrated oxygen acid?

When muriatic acid (HCl) acts on zinc, the metal is taken up, forming ZnCl , and hydrogen is expelled, and if, in place of zinc, oxide of zinc be taken, the effect is the same, except that the hydrogen combining with the oxygen of the oxide forms water; HCl and ZnO giving ZnCl and HO . Now we have in oil of vitriol the elements SO_4H combined together; when put in contact with zinc, H is expelled, and SO_4Zn is formed, and with ZnO and SO_4H , there are produced SO_4Zn , and HO is set free. In both cases, of which the former may be taken as the type of all the haloid salts and the latter of all salts formed by oxygen acids, there is H as the element which is removable by a metal, precisely as one metal is replaceable by another, as indeed from the real metallic character of hydrogen may be considered to occur in this case. Every acid may, therefore, be considered to consist of hydrogen combined with an electro-negative element, which may be *simple*, as chlorine, iodine, fluorine; or may be compound, as cyanogen, NC_2 , and yet capable of being isolated; or as occurs in the great majority of cases, its elements may be such as can only remain together when in combination. Thus oil of vitriol does not contain SO_3 and HO , but consists of hydrogen united to a compound radical SO_4 . Liquid nitric acid does not contain NO_3 and HO , but consists of hydrogen united to a compound radical NO_6 , and the acetic acid is written $\text{C}_4\text{H}_3\text{O}_4 + \text{H}$, the oxalic acid $\text{C}_2\text{O}_4 + \text{H}$, and so on.

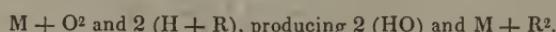
The elegance and simplicity with which the laws of saline combination may be deduced from these principles is really remarkable. Thus it has been remarked as a fact substantiated by experiment, that in neutral salts the number of equivalents of acid were proportional to the number of equivalents of oxygen in the base, but the ordinary theory gave no indication of why this should occur. It follows necessarily from the principles of the newer theory. Thus, if a protoxide be acted on by an acid, M denoting the metal of the oxide, and R the radical of the acid, the resulting action is



and in the neutral salt there is an equivalent of each. Now in the case of a sesqui-oxide, in order that water shall be formed, and so neither acid nor base in excess, the reaction is that



a sesqui-compound being formed perfectly analogous to a sesqui-oxide, and the number of atoms of acid, $3(\text{H} + \text{R})$, is equal to the number of atoms of oxygen in the base (M^2O^3), because that number of atoms of hydrogen are required for the decomposition of the base. In like manner for a deutoxide, there is



The power of salts to replace water in the magnesian sulphates, so as to form double salts, becomes much more intelligible when we compare $\text{H} + \text{O}$ with $\text{K} + \text{SO}_4$, than where H_2O was contrasted with the complex formula $\text{KO} + \text{SO}_3$.

The circumstance that on the new theory (or as it is now often called, the *Binary theory of salts*), it is necessary to admit the existence of a great number of bodies (these *salt radicals*) which have never been isolated, and in favour of whose exist-

ence there is no other proof than their utility in supporting this view, becomes more powerful as an objection, when we proceed to apply its principles to the salts of phosphoric acid. For it has been already described, that this acid forms three distinct classes of salts, all neutral, and which have their origin in the three hydrated states of the phosphoric acid. These states are written on the two views as follows:—

	Old Theory.	New Theory.
Monobasic acid,	$\text{PO}^5 + \text{HO}$	$\text{PO}^6 + \text{H}$
Bibasic acid,	$\text{PO}^5 + 2\text{HO}$	$\text{PO}^7 + \text{H}_2$
Tribasic acid,	$\text{PO}^5 + 3\text{HO}$	$\text{PO}^8 + \text{H}_3$

Now it appears very useless, where the older view accounts so simply for the properties and constitution of these salts, to adopt so violent an idea, as that there are three distinct compounds of phosphorus and oxygen which no chemist has ever been able to detect. But here again other circumstances must be studied; first, the difference of properties of phosphoric acid, in its three states, is totally inexplicable, on the idea of their being merely three degrees of hydration. Nitric acid forms three hydrates, but when neutralized by potash, it always gives the same saltpetre; sulphuric acid forms two perfectly definite hydrates, but with soda forms always the same glauber's salt; whilst phosphoric acid, when neutralized by soda, gives a different kind of salt according to the state it may be in. Also, the permanence of these conditions of phosphoric acid is a powerful proof that they do not consist in the adhesion of mere water. The idea that the phosphoric acid is a different hydracid in each of its three conditions, on the other hand, not merely explains the fact of these differences of properties, but it renders the formation of bibasic and tribasic salts, which is such an anomaly on the old theory, a necessary consequence of the new, for the phosphoric salt radicals, PO^6 , PO^7 , and PO^8 , differ not merely in the quantity of oxygen they contain, but are combined with different quantities of hydrogen, and hence in acting on metallic oxides (bases), there is a different number of atoms required for each to replace the hydrogen and form water. Thus—

PO^6H and NaO give HO and PO^6Na . monobasic phosphate of soda,
 PO^7H_2 and 2NaO give 2HO and PO^7Na^2 . bibasic phosphate,
 PO^8H_3 and 3NaO give 3HO and PO^8Na^3 . tribasic phosphate.

A circumstance which gives additional reason to infer that the water is not merely as base in the phosphoric acid, is the following: if it were so, then it should be most completely expelled by the strongest bases, and the bibasic and tribasic phosphates of the alkalies should be those least likely to retain any portion of the basic water; but the reverse is the fact; whilst oxide of silver, a very weak base, is that which most easily and totally replaces the water. On the idea, however, of hydracids, this is easily understood, for the oxide of silver is one most easily reduced by hydrogen, and consequently one on which the action of a hydrogen acid, as $\text{PO}^3 + \text{H}_3$, or $\text{PO}^7 + \text{H}_2$, would be most completely exercised.

A remarkable verification of this theory has been recently found in the decomposition of solutions of the oxy salts in water, by voltaic electricity. It has been already explained (pp. 314 *et seq.*), that it requires the same quantity of electricity to decompose an equivalent of any binary compound, such as iodide of lead, chloride of silver, muriatic acid, or water. Now, if we dissolve sulphate of soda in water, and pass a current of voltaic electricity through that solution, we have water decomposed, and also the glauber's salt; oxygen and sulphuric acid being evolved at one pole, and soda and hydrogen at the other. Here, on the old view, the electricity performs two decomposing actions at the same time, and, as it thus divides itself, its action on each must be lessened, and the quantity of each decomposed be diminished, so that the sum should represent the proper energy of the current. On measuring these quantities, however, the result is totally different, the quantity of sulphate of soda decomposed is found to be equal to the full duty of the current, and an equivalent of water appears to be decomposed in addition. It is quite unphilosophic to imagine, that the strength of a current should be thus suddenly doubled, and a simple and sufficient explanation of it is found in the new theory of salts. The sulphate of soda in solution having the formula $\text{Na} \cdot \text{SO}^4$ is resolved by the current into its elements, Na and SO^4 , as chloride of sodium would also be; the sodium, on emerging at the negative electrode, from the influence of the current, instantly decomposes water, and soda and hydrogen, of each an equivalent, are evolved; at the positive electrode the compound radical SO^4 also decomposes water, and produces $\text{H} \cdot \text{SO}^4$ and O . The appearance of the oxygen and hydrogen is thus but secondary, and the body really decomposed by the current is only $\text{Na} \cdot \text{SO}^4$.

In the case of the salts of such metals as do not decompose water, the phenomena

are much more simple. Thus a solution of sulphate of copper, when decomposed by the battery, yields metallic copper at the negative, and sulphuric acid and oxygen at the positive electrode, and the quantity of copper separated represents exactly the energy of the current which has passed, for the salt being $\text{Cu}.\text{SO}_4$, is simply resolved into its elements, but SO_4^4 reacting on the water, produces $\text{H}.\text{SO}_4$ and O at the positive electrode. On the old view, it was supposed that water and sulphate of copper were both decomposed, oxygen and acid being evolved at one side, and oxide of copper and hydrogen being separated at the other; which reacting produced water and the metal. Such an explanation, however, is directly opposed to the law of the definite action of electricity, and cannot be received.

In the case of solutions of chlorides or iodides, where there can be no doubt of the relations of the elements, the results of voltaic decomposition are precisely similar. Chloride of copper gives simply chlorine and copper, no water being decomposed. Chloride of sodium or iodide of potassium give chlorine or iodine at the one electrode, and alkali and hydrogen at the other; the evolution of these last being caused by the action of the metallic basis on the water of the solution.

Professor Daniell, to whom these important electro-chemical researches are due, considers the truth of the binary theory of salts to be fully established by them.

If this theory be adopted, a profound change in our nomenclature of salts will become necessary. Graham has proposed that the name of the salt radical should be formed by prefixing to the word *oxygen* the first word of the ordinary name of the class of salts, and that the salts be termed by changing *oxygen* into *oxides*. Thus SO_4^4 , *sulphatoxygen*, gives sulphatoxides, the sulphates. NO_6^6 , *nitratoxygen*, gives nitratoxides, the nitrates, and so on; but I consider that the form of nomenclature proposed by Daniell deserves the preference. It has been described (p. 314), that Faraday proposed to term the elements which pass to the electrodes of the battery, *ions*; acting on this, Daniell proposes to term the electro-negative element of the sulphates *oxysulphion*, that of the nitrates *oxynitrition*, and so on, and the salts may be termed *oxysulphion* of copper, *oxynitrition* of sodium, &c. It would be desirable, however, for a long time, to introduce these names only where theoretical considerations rendered their employment decidedly useful, and hence, in all future description of the salts, I shall make use of the language of our ordinary views, and treat of their preparation and composition without any reference to the discussion in which we have been engaged.

The general adoption of the binary theory of salts has deprived of much of its interest and importance a question, which some years since was very ingeniously discussed, viz.—whether, in the formation of double salts, the salts which unite had the same relation to each other that acid and base were then thought to have. Thus it was supposed that the electro-negative qualities of sulphuric acid being less controlled by oxide of copper than by potash, the alkaline sulphate acted as a base to the sulphate of copper, when these two salts combined to form the double sulphate of potash and copper, and so on in other instances; but in addition to the circumstance that all we have said as to the constitution of the salts militates against this view, we have the positive evidence that, first, these double salts are formed not by combination merely, but by replacement of the constitutional water of the sulphates of the copper or magnesian class, which water nobody would contend to act in them as a base; and second, that when a solution of such a double salt is decomposed by the battery, the two salts are not separated as if they were acid and base, but are decomposed independently in the proportions of an equivalent of each, making together the sum of the chemical energy of the current.

A similar idea was advocated by Bonsdorff regarding the double chlorides, iodides, &c. He proposed to consider the chlorides of gold, platina, mercury, &c., as chlorine acids, and those of potassium, &c., as chlorine bases, and so with the iodides. This view, however, although at first very extensively adopted, has given way to the gradual growth of knowledge. There is no analogy between a dry oxygen acid and a chloride; but the chlorides are in perfect analogy with the neutral salts. Thus CuCl does not resemble SO_3^3 , but $\text{Cu}.\text{SO}_4^4$ and $\text{CuCl} + \text{KCl}$ is analogous not to SO_3^3KO , but to the double salt $\text{Cu}.\text{SO}_4^4 + \text{K}.\text{SO}_4^4$. Bonsdorff's idea was exactly counter to the direction of truth; he sought to bring all salts under the one head, by extending to all the constitution of oxygen acids and oxygen bases, whilst the progress of science has led us to the opposite generalization of reducing all salts to the simple haloid type."